Sample NCEM proposal

Proposal Title: "Surface and interfacial structures of nanocrystals"

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Summary: The goal of this study is to develop a technique to reconstruct the 3-D atomic structure of the surface and interface of individual supported nanoparticles using a combination of geometric phase analysis (GPA) [1], single particle nano-probe diffraction (NPD) and simulation [2]. The atomic structure of nanoparticles' surfaces is of immediate use in understanding the surface chemistry of supported nanoparticles that form the basis of the multi-billion dollar catalysis industry. As an example, we have chosen to investigate the model catalytic system of Au-TiO_2 that catalyzes the conversion of CO to CO_2 [3]. We propose to use the TEAM instrument to perform high resolution imaging experiments of Au nanocrystals on TiO_2 substrates.

Scientific Motivation: The atomic structure of nanoparticle surfaces is of great importance for catalysis, yet poorly understood. The goal of this study is to develop a technique to reconstruct the 3-D atomic structure of the surface and interface of individual supported nanoparticles using a combination of geometric phase analysis, single particle nano-probe diffraction and simulation. In each case, state-of-the-art structure determination will complement the high-resolution imaging to provide a framework for the analysis of nanoparticle surface structures through electron microscopy.

Technical Feasibility: The starting point of this study is a unique sample preparation technique that consists of making thin and pristine single crystal TiO_2 surfaces (Figure 1) onto which nanoparticles can be loaded repetitively on the same plane of TiO_2. In this cross-sectional geometry, the electron beam travels only through the nanoparticle thus eliminating any interference effects with the substrate (Figure 2). Further, by eliminating the polymeric materials used in conventional cross-sectional TEM sample preparation, a high signal to noise ratio is achieved in the diffraction patterns. Since the particles are firmly attached to the substrate they pose no risk to environment, health and safety from exposure to engineered nanoparticles. The sample is compatible with the TEAM 0.5 microscope and ideal for the HRTEM imaging proposed here.

Need for NCEM's unique or advanced facilities: Figure 3 shows a HRTEM image of a gold nanoparticle taken at the user's institution using a JEOL 2010FEG. It is seen that the surface and interface atoms of the gold nanoparticle appear fuzzy due to microscope's aberrations and the consequent electron wavefunction delocalization. However, to verify the results from the coherent diffraction experiments and simulation, changes in lattice positions of the order of 0.05 Å need to be resolved with confidence. This can be

achieved with GPA provided the image has a much higher quality. Therefore a microscope with much better point-to-point resolution as well as reduced delocalization is sought. The TEAM microscope is well suited to this need. The higher quality images can facilitate the measurement of changes in atomic positions of the order of ~0.05 Å using GPA.

Experience of the research group required to achieve the proposal's goals: The user has over 300 hours of hands on TEM experience and is proficient with JEOL 2010 FEG, JEOL 2010 LaB_6, JEOL 2100 LaB_6 and Philips CM-12 microscopes. The group's major focus has been high resolution microscopy, nanodiffraction, in-situ heating experiments and simulation of nanodiffraction patterns for the past ten years.

Availability of NCEM resources needed to support the proposed work: The dominant epitaxies observed with Au on TiO_2 are:

Au(111) || TiO_2(110)
Au(224) || TiO_2(110)
Au(200) || TiO_2(110)

The lattice spacings of Au (222) – 1.44 Å, Au (224) – 0.83 Å and Au (200) – 2.04Å are thus easily resolvable with the capabilities of the TEAM 0.5 microscope. Further, since the delocalization in the TEAM images is minimal, even a 0.05 Å change in lattice spacing should still resolvable with confidence. We intend to use the TEAM 0.5 microscope for a number of imaging and nanoprobe diffraction sessions and perform the simulations at our home institution. We only anticipate examining one size of Au nanoparticles and the samples will be pre-screened in a microscope at UIUC.

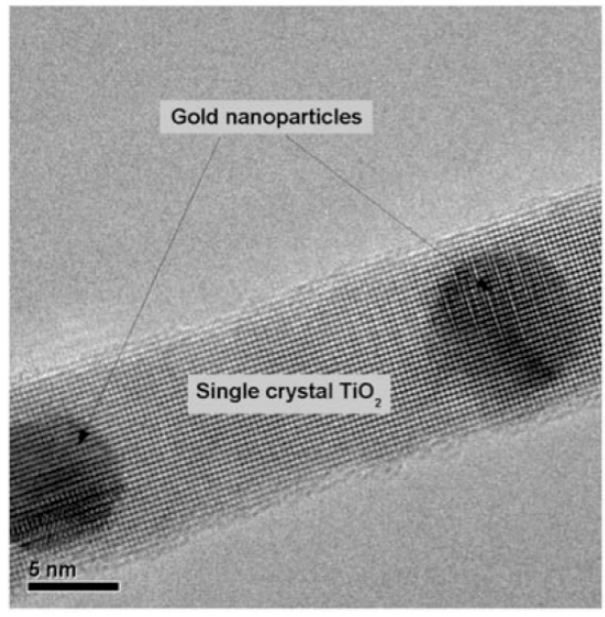

Figure 1: Thin and pristine single crystal TiO_2

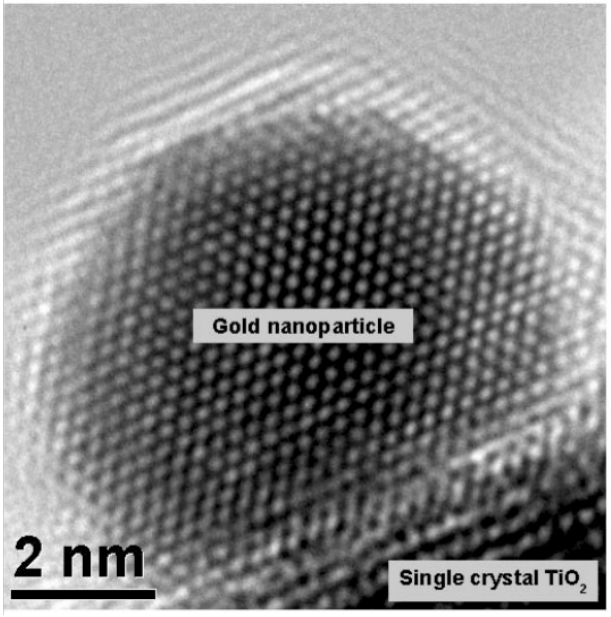

Figure 2: Au nanoparticle supported on single crystal TiO_2 (110)

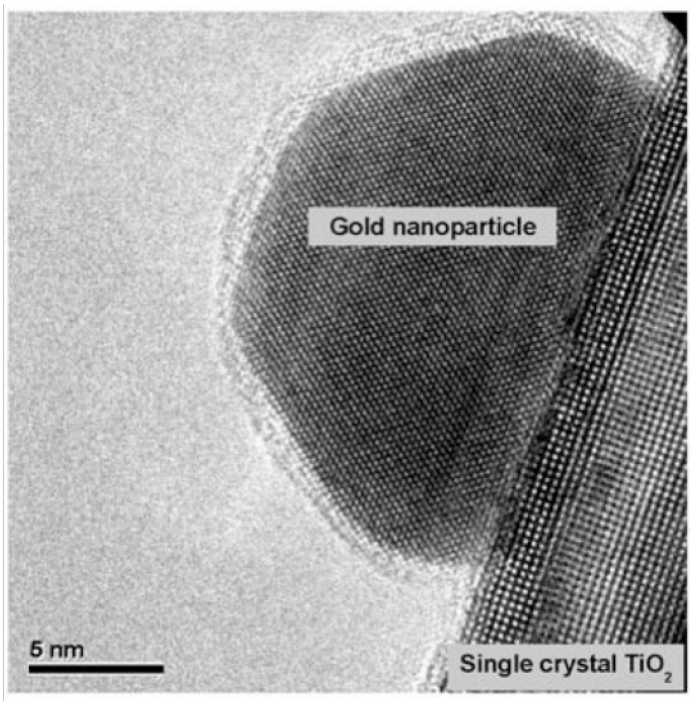

Figure 3: HRTEM image showing the surface and interface of Au- TiO_2 (110)

References:

[1] "Quantitative measurement of displacement and strain fields from HREM micrographs", M.J. Hytch, E. Snoeck, R. Kilaas, Ultramicroscopy 74, 131-146 (1998)

[2] "Coordination-dependent surface atomic contraction in nanocrystals revealed by coherent diffraction", W.J. Huang, R. Sun, J. Tao, L.D. Menard, R.G. Nuzzo & J.M. Zuo, Nature Materials 7, 308 - 313 (2008)

[3] "Low-temperature oxidation of CO over gold supported on TiO_2, alpha-Fe_2O_3 and Co_3O_4", M. Haruta, S.Tsubota, T. Kobayashi, H. Kageyama, M.J. Genet, B. Delmon, Journal of Catalysis 144, 1, 175-192 (1993)